

## Conformational Analysis. Part XLIII. $^{13}\text{C}$ Chemical Shifts and Coupling Constants as Proof of the Nonplanarity of the 2-Oxo-1,3-dioxolane Ring<sup>1,2</sup>

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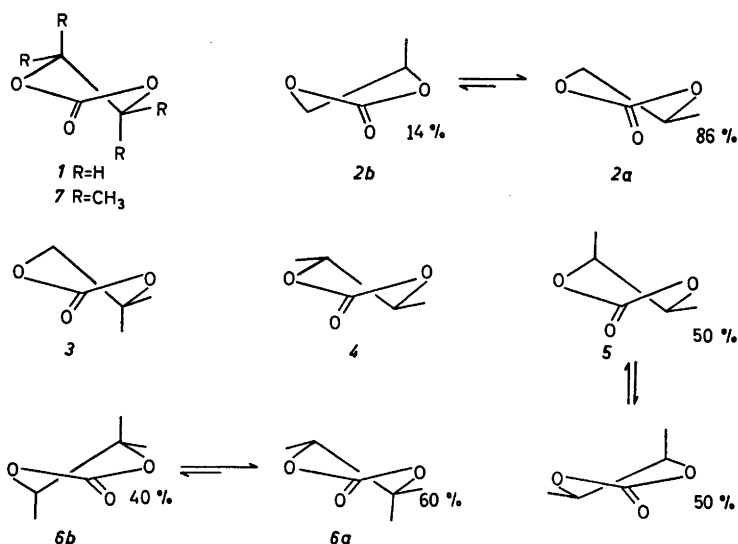
The  $^{13}\text{C}$  chemical shifts and coupling constants for 2-oxo-1,3-dioxolane and its methyl-substituted derivatives are reported. Substituent effects on the chemical shifts are derived and their type and magnitude discussed with respect to the ring geometry and other conformational factors. The results are best explained with a half-chair conformation where the bond joining C4 and C5 bisects the  $\text{CO}_2$  plane.

It is well documented<sup>3-7</sup> that for a series of compounds with similar conformations

$$\delta\text{C}(x) = \delta_p\text{C}(x) + \sum\text{SE}(x) \quad (1)$$

where  $\delta\text{C}(x)$  is the chemical shift of the  $x$ th carbon atom in any given derivative,  $\delta_p\text{C}(x)$  the chemical shift of the same carbon atom in the parent compound and  $\sum\text{SE}(x)$  the sum of the different substituent effects influencing it. Keeping this in mind  $^{13}\text{C}$  chemical shifts may be helpful in removing the controversy still existing with respect to the ring conformation of 2-oxo-1,3-dioxolanes.<sup>8-18</sup>

Brown<sup>8</sup> pointed out by the X-ray method that the crystalline 2-oxo-1,3-dioxolane (*1*) is not planar but the line joining C4 to C5 makes



Scheme 1.

Table 1.  $^{13}\text{C}$  chemical shifts ( $\delta$ ) for the 2-oxo-1,3-dioxolanes studied.

Compound	Substitution	C2	C4	C5	C(Me)
1	Nil	156.07	65.10	65.10	—
2	4-Me	155.22	73.75	70.82	19.36
3	4,4-Me <sub>2</sub>	154.64	81.80	75.37	25.92
4	<i>trans</i> -4,5-Me <sub>2</sub>	154.77	80.05	80.05	18.26
5	<i>cis</i> -4,5-Me <sub>2</sub>	154.77	76.21	76.21	14.29
6	4,4,5-Me <sub>3</sub>	154.18	84.21	81.48	25.66(4), 20.92(4), 14.49(5)
7	4,4,5,5-Me <sub>4</sub>	153.92	86.09	86.09	22.35
8	1,3-Dioxolane <sup>3</sup>	95.23	64.81	64.81	—

an angle of  $20^\circ$  with the plane containing the  $\text{CO}_2$  group. Angell<sup>10</sup> and Simon and Heintz<sup>11</sup> studied the same compound in the liquid state by IR and Raman spectroscopy and stated their results with a planar structure and  $C_{2v}$  symmetry. Finegold<sup>12</sup> assumed the 4-methyl-2-oxo-1,3-dioxolane ring (2) planar though he did not refer to earlier reports. Paasivirta<sup>13,14</sup> studied the  $^1\text{H}$  NMR spectra of some chlorinated 2-oxo-1,3-dioxolanes and interpreted his results with a half-chair structure. Petrick *et al.*<sup>15</sup> concluded from NMR, IR and ultrasonic absorption measurements that 1, 2 and 4-chloromethyl-2-oxo-1,3-dioxolane have similar ring conformations though they do not mention any shape. Petrick<sup>15,16</sup> also refers to a microwave measurement<sup>17b</sup> which is nonexistent since Arbusov studied<sup>17a</sup> dipole moments instead. Wang *et al.*,<sup>18</sup> however, studied the microwave spectrum of 1 in the gaseous state and their results were best explained with a nonplanar ring and  $C_2$  symmetry.<sup>3</sup>

In the present work we determine the  $^{13}\text{C}$  chemical shifts for 2-oxo-1,3-dioxolane (1) and its methyl-substituted derivatives 2–7 and from them the substituent effects on the ring carbon atoms. In some cases we also determine the values of the various coupling constants for further clarification of the actual shape of these molecules.

## EXPERIMENTAL

2-Oxo-1,3-dioxolane (1) and its methyl derivatives 2–7 were prepared conventionally<sup>19</sup> and proved to be identical with authentic samples by IR, NMR and physical constants.<sup>19–21</sup>

The  $^{13}\text{C}$  NMR spectra were recorded on a JEOL FX-60 FT NMR spectrometer for 14–15% (w/w)  $\text{CDCl}_3$  solutions at 298 K. The chemical shifts ( $\delta$ ) and coupling constants are given in Table 1.

Two sets of 6 to 8 simultaneous equations (eqn. 1) with unknown SE's were solved on a DEC-10 computer by the use of a multiple linear regression analysis.<sup>22</sup> The conformationally inhomogeneous compounds (2, 5 and 6) were treated as being composed of appropriate mol fractions of the two conformers (Scheme 1). These mol fractions were obtained in an iterative manner to find out the best fit for the substituent effect correlations (Table 2).

Table 2. Substituent effects on the  $^{13}\text{C}$  chemical shifts of methyl-substituted 2-oxo-1,3-dioxolanes.

Substitution	Substituent effect on the ring carbon atom	
	C2	C4 <sup>a</sup>
4e-Me	$-0.88 \pm 0.06$	$8.66 \pm 0.01$
4a-Me	$-0.59 \pm 0.09$	$8.66 \pm 0.01$
5e-Me	$-0.88 \pm 0.06$	$5.72 \pm 0.01$
5a-Me	$-0.59 \pm 0.09$	$5.72 \pm 0.01$
4,4-Me <sub>2</sub>	—	$-0.61 \pm 0.01$
5,5-Me <sub>2</sub>	—	$-1.18 \pm 0.01$
4e5e-Me <sub>2</sub>	$0.44 \pm 0.12$	$0.57 \pm 0.01$
4e5a-Me <sub>2</sub>	$0.15 \pm 0.09$	$-1.35 \pm 0.04$
4a5e-Me <sub>2</sub>	$0.15 \pm 0.09$	$-5.20 \pm 0.04$
Standard deviation of fit		
in ppm:	0.07	0.01
Chemical shift range:	2.15	20.99

<sup>a</sup> Due to the symmetry of the 2-oxo-1,3-dioxolane ring substituent effects on C5 are equal to those on C4 if 4 and 5 are interchanged in the substitution column.

8.65 = SE(4)							
5.72 =	SE(5)						
16.70 = 2SE(4)		+ SE(4,4)					
10.27 =	2SE(5)		+ SE(5,5)				
14.95 = SE(4)	+ SE(5)			+ SE(4e5e)			
11.11 = SE(4)	+ SE(5)				+ 0.5SE(4e5a)	+ 0.5SE(4a5e)	
19.11 = 2SE(4)	+ SE(5)	+ SE(4,4)		+ 0.6SE(4e5e)	+ 0.4SE(4e5a)	+ 0.6SE(4a5e)	
16.38 = SE(4)	+ 2SE(5)		+ SE(5,5)	+ 0.6SE(4e5e)	+ 0.6SE(4e5a)	+ 0.4SE(4a5e)	
20.99 = 2SE(4)	+ 2SE(5)	+ SE(4,4)	+ SE(5,5)	+ SE(4e5e)	+ SE(4e5a)	+ SE(4a5e)	

*Eqns. 2.*

RESULTS AND DISCUSSION

Substituent effects on C4 and C5

If the 2-oxo-1,3-dioxolane ring has the half-chair conformation<sup>8</sup> in solution the methyl substituents should have more or less equatorial and/or axial character. It was relatively easy to determine that the best fit for the set of equations (2) was obtained when SE(4e) = SE(4a), SE(5e) = SE(5a) but SE(4e5e) ≠ SE(4a5a) = 0, SE(4e5a) ≠ SE(4a5e).

Due to symmetry *cis*-4,5-dimethyl-2-oxo-1,3-dioxolane (5) includes equal amounts of the 4e5a and 4a5e conformations (Scheme 1). The Δδ values of 4,4,5-trimethyl derivative (6) in comparison with those of 5 and 7 led to the conclusion that it is not conformationally homogeneous but includes both 4e4a5e (6a) and 4a4e5a (6b) forms. By an iterative method it was found that the best fit for eqn. 2 was obtained when 6 consisted of 60 % of 4e4a5e (6a) form. At this stage one may argue that the *trans*-4,5-dimethyl derivative (4) also consists somewhat of the diaxial conformation. However, this compound can easily be compared with 6, minimize the 4e5e *gauche* interaction without existing appreciably in the 4a5a conformation. At any rate the amount of the diaxial form is clearly less than 10 %.

Eqns. 2 which assume that the 2-oxo-1,3-dioxolane ring has the half-chair conformation led to an excellent fit between the observed and calculated chemical shifts. This is, of course, partly due to the limited number of the methyl-substituted derivatives when compared with the amount of different substituent effects

(Table 2). However, we consider our results confirmatory to the report of Brown<sup>8</sup> who presented a half-chair structure for the 2-oxo-1,3-dioxolane ring in the crystalline state.

From the conformational equilibrium of 6 we can further estimate the conformational energy of the axial methyl group if we assume that the *gauche* interactions between the methyl groups have the normal value, 3.6 kJ mol<sup>-1</sup>. At 298 K -ΔG° (4a-Me) = 3.6 + RT ln K (K = 1.5) = 4.6 ± 0.5 kJ mol<sup>-1</sup>. From this result we estimate that 2 is actually an 86:14 mixture of the equatorial (2a) and axial (2b) forms which result we need when deriving the substituent effects on C2.

Substituent effects on C2

Substitution of the 2-oxo-1,3-dioxolane ring does not have much influence on the chemical shift of C2. However, these influences are again clearly dependent on the spatial arrangement of the C4-C5 fragment of the molecule (*cf.* Tables 1 and 2). After some trials eqns. 3 were found to give an excellent fit between the observed and calculated chemical shifts of C2.

This result again supports the view that the predominant conformation of the 2-oxo-1,3-dioxolane ring in solution is a half-chair form similar to that in the crystalline state. The chemical shifts of C2 are normal for carbonate carbons whereas that of C4 and C5 in 1 is only slightly different from the value determined<sup>8</sup> for the same carbon atoms in the 1,3-dioxolane ring (Table 1) in agreement with the postulate that both rings are nonplanar and resemble

-0.85 = 0.86SE(4e)	+ 0.14SE(4a)		
-1.43 = SE(4e)	+ SE(4a)		
-1.30 = 2.00SE(4e)		+ SE(4e5e)	
-1.30 = SE(4e)	+ SE(4a)	+ SE(4e5a)	
-1.89 = 1.60SE(4e)	+ 1.40SE(4a)	+ 0.60SE(4e5e)	+ SE(4e5a)
-2.15 = 2.00SE(4e)	+ 2.00SE(4a)	+ SE(4e5e)	+ 2SE(4e5a)

*Eqns. 3.*

Table 3. One-bond, geminal and vicinal coupling constants.

Compound	$J_{\text{CH}}/\text{Hz}$	$J_{\text{CCH}}/\text{Hz}$	$J_{\text{COCH}}/\text{Hz}$
1	156.2		
2	156.2 (4)	3.9	2.9
	154.3 (5)	5.5	
	127.9 ( $\text{CH}_3$ )	4.4	
4	153.3 (4,5) <sup>a</sup>	4.4	2.4
	127.9 ( $\text{CH}_3$ )	3.9	
5	154.3 (4,5) <sup>b</sup>	4.4	2.4
	127.9 ( $\text{CH}_3$ )	1.95	

<sup>a</sup> $J_{\text{CHax}}$ . <sup>b</sup> $0.5J_{\text{CHax}} + 0.5J_{\text{CHeq}}$ . Thus  $J_{\text{CHeq}} = 155.3$  Hz.

each other in the C(4)–C(5) range. This conclusion is verified by the fact that an oxo substituent at position 5 of the 1,3-oxathiolane ring changes the chemical shift of C2 by 4.22 ppm and that of C4 by 1.88 ppm as a consequence of the conformational change from a favoured C(5) envelope form to an S(3) envelope form.<sup>23</sup>

#### Coupling constants

Further evidence for the half-chair structure can be obtained from the values of the various coupling constants (Table 3). The one-bond,  $J_{\text{CH}}$ , couplings already point out, e.g., that 4 and 5 have the ee and ea configurations, respectively, since  $J_{\text{CHax}} = 153.3$  Hz and  $J_{\text{CHeq}} = 155.3$  Hz in agreement with other related observations in this laboratory.<sup>23</sup> The same situation is revealed even more strikingly from the geminal  $J_{\text{CCH}}$  coupling constants between  $\text{CH}_3(4)$  and  $H(4)$  since for 4  $J_{\text{CCHax}} = 3.9$  Hz and for 5  $J_{\text{CCHeq}} = 2(J_{\text{CCH}}^{\text{obs}} - 0.5J_{\text{CCHax}}) = 0$ .

#### Conclusion

As a result of our analysis of the chemical shifts and coupling constants of 2-oxo-1,3-dioxolane 1 and its methyl derivatives 2–7 we conclude that the ring exists predominantly in a half-chair conformation where the C4–C5 bond bisects the  $\text{CO}_2$  plane. This result is in close agreement with the X-ray<sup>9</sup> and microwave<sup>18</sup> results as well as with the postulates of Paasivirta,<sup>13,14</sup> Arbusov<sup>17a</sup> and Pethrick *et al.*<sup>15,16</sup> However, our results do not lend any support to those reports<sup>10–12</sup> which suggest

a planar ring in 2-oxo-1,3-dioxolane 1. Finally we were able to show that the equatorial-axial preference for a methyl group in the studied compounds is  $4.6 \pm 0.5$  kJ mol<sup>-1</sup> at 298 K.

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