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NMR EXPERIMENTS ON ACETALS—57

CONFORMATIONAL STUDY OF 5-ALKYLIDENE-1,3-DIOXANES

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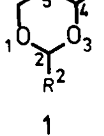
Abstract—From an extensive ^{1}H-NMR comparative study (homo-INDOR-, and nmdr-assisted) of a series of 2-, 4- and 2,4-substituted 5-alkylidene-1,3-dioxanes it is concluded that the basic conformation is a flattened chair (Fig. 5c,f). This is substantiated by the low barrier to ring reversal in 5-methylidene- and 5-propylidene-1,3-dioxane of $\Delta G^{\neq} \sim 5{\cdot}5$ kcal/mole (T_c resp. −158° and −161°).

INTRODUCTION

The presence of an *exo* double bond at C-5 in 1,3-dioxane is expected to bring about the same conformational changes with respect to the basic chair form of the system as it does in c.hexane. Indeed, there is no mesomeric overlap possible between the π-bond and the ring O-atoms, as it would be the case in the 4-position,[1] but on the other hand the synaxial H/p-lobe interaction, originally present in 1,3-dioxane, has been changed into a π/p-lobe remoted interaction.

It was therefore interesting to study the 5-alkylidene-1,3-dioxanic system, the more so, because previous reports showed 5-methylidene-1,3-dioxane still at −110° extremely mobile,[2] and no clear-cut data concerning either the ring shape or barriers to ring reversal were obtained.

We therefore prepared a series of (substituted) 5-alkylidene 1,3-dioxanes (structures **1A** to **I**) and undertook an ^{1}H-NMR study at variable temperatures and in different solvents. We have also studied the *cis* and *trans* isomeric reduction products of **1G-I**, i.e. the 4,5-diMe- and 2,4,5-triMe-1,3-dioxanes. The ^{1}H-NMR-parameters obtained are gathered in Tables 1–3.



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A: $R^2 = R^4 = R^5 = R'^5 = H$
B: $R^2 = Me$; $R^4 = R^5 = R'^5 = H$
C: $R^2 = R'^2 = Me$; $R^4 = R^5 = R'^5 = H$
D: $R^2 = R^4 = H$; $R^5 = R'^5 = Me$
E: $R^4 = H$; $R^2 = R^5 = R'^5 = Me$
F: $R^4 = H$; $R^2 = t\text{-Bu}$; $R^5 = R'^5 = Me$
G: $R^2 = R^5 = R'^5 = H$; $R^4 = Me$
H: $R^5 = R'^5 = H$; $R^2 = R^4 = Me$[*cis*]
I: $R^5 = R'^5 = H$; $R^2 = R^4 = Me$[*trans*]

RESULTS AND DISCUSSION

The 2-Me-, resp. 2-t-Bu groups are believed to anancomerize the system, except perhaps when counterbalanced by an additional 4(6)-*trans*-Me substituent. Also the mono 4-Me-substituted derivative is believed to represent a one-sided situation of the equilibrium state between (two) possible inverting conformations. Indeed, in the saturated system, the conformational energies for C-2 and C-4 substitutions are so high, that even in possible more flexible systems than in the present case, their values still remain high enough (e.g. in 1,3-dioxane: $\Delta G°(\text{Me-2}) = 4{\cdot}1 - 4{\cdot}3$ kcal/mole;[4] $\Delta G°$ (Me-4) $= 2{\cdot}8 - 2{\cdot}9$ kcal/mole).[4,5] We have ascertained the equatorial nature of the 4-Me group in 4-Me-5-methylidene-1,3-dioxane by a comparative reduction study between **1G** and **1H** (see later under heading: reduction).

We may therefore rely upon the NMR-data obtained in the spectrum of the model compounds **1B**, **1E**, **1F**, **1G** and **1H** as representative of the main conformation of the 5-alkylidene-1,3-dioxanic system. There are several good indications that this form is not a boat-twist and certainly not a classical boat form. We found that H-2a absorbs systematically at 0·05–0·2 ppm lower field than in the corresponding saturated compounds,[3,6] and the same is generally true for the Me-2 substituent. This is difficult to reconcile with a classical boat form, because the presence of the *exo* double bond would certainly shield the H-2 and Me-2 protons (Fig. 1A). 2,5-Twist-boat conformations (e.g. Fig. 1B) are unlikely because $^2J2$ in **1G** is −6·2 Hz,* a value which can only fit either a classical boat (which is excluded) or a chair conformation.[7,8] Also $^2J6$ (in **1B**, **1E**, **1F**, **1H** and **1I**; see Table 2) is −12·4/−13·1 Hz, in comparison with the value for chair 1,3-dioxanes, where it is −11·5 Hz[11] (see also Table 3). The value, more negative by −0·9/−1·6 Hz in the present compounds, is the result of the influence of the adjacent π-bond (Barfield–Grant effect[12]). We therefore may conclude that the main conformation is a flattened chair.

In 4,4-dideutero methylidene-cyclohexane, the negative contribution caused by the π-system is only −0·1/−0·2 Hz. This is almost the effect[13] expected because of the geometry of this compound as it was deduced by Bucourt,[14] for which torsion angles of 51° at the positions next to the exocyclic double bond have been proposed (Fig. 2A). The Barfield–Grant effect of −0·9/−1·6 Hz in the 5-alkylidene-1.3-dioxanic system suggests a more flattened moiety, e.g. torsion angles of 40–45° (Fig. 2B). This is further substantiated by the size of the allylic coupling values $^4J^t(6e,5)$ and $^4J^c(6e,5')$ of *ca.* −0·5 Hz, which is in accordance with a ϕ-value (Fig. 2B) of *ca.* 105°.[15-17] The values of $^4J^t(6a,5)$ and $^4J^c(6a,5') = -1{\cdot}5$ Hz are somewhat small in comparison with the proposed ϕ-value of 345°

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*There is a small dependence of $^2J2$ on the solvent, becoming slightly more negative the more polar the medium is. This is a normal trend, and has been recognized as a contribution of a "reaction-field";[9,10] e.g. for 1G $^2J2(C_6D_6) = -6{\cdot}20$ Hz; $^2J2(\alpha\text{-Cl-naphth}) = -6{\cdot}30$ Hz.

Table 1. Shift-data (in ppm, TMS internal) of 5-alkylidene-1,3-dioxanes[a]

		H-2e(Me-2)	H-4(Me-4)	H-5(Me-5)	H-5'(Me-5')	H-6a	H-6e	H-2a(Me-2')	Others
1A	CCl$_4$	4.74	4.16	4.79	4.79	4.16	4.16	4.74	
1B	CCl$_4$	(1.23)	see H-6	4.83	4.83	4.17	4.21	4.68	
	C$_6$D$_6$	(1.34_5)	see H-6	4.52	4.52	3.87	4.03	4.50	
1C	CS$_2$	(1.27)	see H-6	4.66(q)	4.66(q)	4.11(t)	4.11(t)	(1.27)	
1D	CS$_2$r.t.	4.67	see H-6	(1.61 q)	(1.61 q)	4.23	4.23	4.67	
	CS$_2$ (-90°)	4.61		(1.64 q)	(1.64 q)	4.16	4.16	4.61	
1E	CCl$_4$	(1.35)	see H-6	(1.65)	(1.65)	3.92	4.51	4.51	
1F	CS$_2$	-	see H-6	(1.65)	(1.65)	3.96	4.60	4.02	t.Bu : 0.81
1G	CCl$_4$	4.94	4.12 (1.33)	4.84	4.84	4.11	4.21	4.70	
	CDCl$_3$	4.94	4.12 (1.34)	4.84_5	4.84_5	4.11	4.23	4.71	
	C$_6$D$_6$	5.00	3.91 (1.24)	4.64	4.58_5	3.91	4.14	4.56_6	
	α-Cl-Napht.	5.09	3.67 (1.12)	4.47	4.44_7	3.78	4.09	4.52	
1H	CCl$_4$	(1.24)	4.13 (1.32)	4.85	4.85	4.14	4.20	4.74_5	
	CDCl$_3$	(1.35)	4.26_5(1.39)	4.94	4.93	4.28	4.31_5	4.89	
	(95%) C$_6$D$_6$	(1.35)	3.93 (1.24)	4.65	4.58_5	3.97	4.14	4.64_5	
1I	CDCl$_3$	(1.31)	4.59 (1.44)	4.89	4.89	4.24_5	4.45	5.10_5	

(a) At 300 MHz except for low temperature (60MHz).

Table 2. Coupling constants (in Hz) of 2-Me-5-methylidene-1,3-dioxane (1B); 2-t-Bu-5-propylidene-1,3-dioxane (1F); 2-Me-5-propylidene-1,3-dioxane (1E); 4-Me-5-methylidene-1,3-dioxane (1G); 2,4-*cis*-diMe-5-methylidene-1,3-dioxane (1H) and 2,4-*trans*-diMe-5-methylidene-1,3-dioxane (1I). Values and signs confirmed by simulation (SIMEQ 16/II) and nmdr techniques

Compound J	1B CDCl$_3$	1B C$_6$D$_6$	1E CCl$_4$	1F CS$_2$	1G CCl$_4$	1H C$_6$D$_6$	1H CDCl$_3$	1G C$_6$D$_6$	1I CDCl$_3$
^{2}J2					- 6.2			- 6.2	
^{2}J4(6)	--	-13.1	-12.9	-13.1	-12.4	-12.4	-12.4	-12.3	-13.0
^{2}J5					--	- 0.7	- 0.5	- 0.7	
^{3}J(2,Me2)	5.05	5.05	5.0		5.1	5.1	5.1		4.9
^{3}J(4,Me4)					6.4	6.4	6.3	6.4	6.9
^{4}J2a,4e	(-0.2)[a]	- 0.2							
^{4}J2a,6e	(-0.2)[a]	- 0.2							
^{4}J2e,6a					- 0.7			-0.5	
^{4}J2e,6e					- 0.8[b]			-0.8	
^{4}J2e,4a					- 0.7			-0.5	
^{4}J4a,6a					- 1.4	- 0.7	- 1.4	-0.8	
$^4J^t$4a,5					- 1.5	- 1.6	- 1.5	-1.6	
$^4J^c$4a,5'					- 1.5	- 1.6	- 1.3	-1.6	
^{4}J 4a,6e							- 0.6		
$^4J^t$6a,5	(-1.05)[a]	- 1.5			- 1.5	- 1.6	- 1.5	-1.6	
$^4J^c$6a,5'	(-1.05)[a]	- 1.5			- 1.5	- 1.6	- 1.3	-1.6	
$^4J^t$6e,5	(-1.05)[a]	- 0.4			- 0.4	- 0.4	- 0.5	-0.4	
$^4J^c$6e,5'	(-1.05)[a]	- 0.4			- 0.4	- 0.4	- 0.5	-0.4	
^{5}J Me4,5						- 0.1	- 0.1		
^{5}J Me4,5'						- 0.1	- 0.15		
^{5}J Me5,4a			+ 1.4	+ 1.4					
^{5}J Me5,4e			+ 0.35	+ 0.35					

(a) Apparent coupling values (deceptive simple 4,6-pattern).

(b) Ascertained by homo INDOR experiments at 100 MHz.

Table 3. ^{1}H-NMR data for *trans*-4,5-diMe-1,3-dioxane (2); *r*-2, *cis*-4, *trans*-5-triMe-1,3-dioxane (3) *cis*-4,5-diMe-1,3-dioxane (4) and *r*-2, *cis*-4, *cis*-5-triMe-1,3-dioxane (5) in CCl_4 at 100 MHz. Shifts in δ, J in Hz (see Refs. 3 and 6)

Comp. / Shifts	2	3	4	5	Comp. / J	2	3	4	5
Me-2	-	1.20	-	1.20	$^2J2$	-5.9	-	-5.9	-
Me-4	1.15	1.16	1.07	1.07	$^2J6$	-11.0	-11.2	-11.1	-11.0
Me-5	0.69_5	0.70	1.04	1.05	$^3J4a,5a$	9.8	9.8	-	-
H-2a	4.46	4.53	4.51_5	4.55	$^3J4a,5e$	-	-	2.5	3.4
H-2e	4.81	-	4.80_5	-	$^3J5a,6a$	11.1	11.0	-	-
H-4a	3.13	3.17	3.71	3.77	$^3J5a,6e$	4.5	4.6	-	-
H-5a	1.56	1.51	-	-	$^3J5e,6a$	-	-	2.6	3.4
H-5e	-	-	1.30	1.28	$^3J5e,6e$	-	-	1.8	1.6
H-6a	3.07	3.11_5	3.69	3.73_5	$^3JMe2,2$	-	5.1	-	5.1
H-6e	3.80	3.80	3.69	3.73_5	$^3JMe4,4$	6.1	6.1	6.6	6.4
					$^3JMe5,5$	6.9	6.7	6.9	6.9

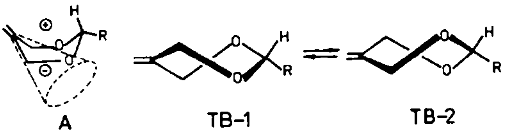

Fig. 1.

(Fig. 2B), but in several cases this trend has been observed.[16] It may well be, that the trigonal projection angles of 120° used in our model construction are too simplified and semi-quantitative predictions are therefore satisfying.

computerized energy calculations, Bucourt has found[18,21] that a typical deformation in one of the bonds, results in a deformation of the same sign of about 60% in the adjacent bonds, but of opposite sign of resp. 10% and 30% in the bond further removed (see Fig. 2C). In order to predict therefore the torsion angles in 5-methylidene-1,3-dioxane one may proceed in two ways. Either we take the typical torsion values in *c*.hexane, i.e. 56°,[22] and we introduce the assumed flattening to 43°, or we start from values in 1,3-dioxane, i.e. 54°/55°.[23] This gives us the values shown in Fig. 3 under respectively **b** and **e**, with torsion angles of respectively 59° (*c*.hexane model) and 66° (1,3-dioxane model) around C_2–O. The value of $^2J2 = -6{\cdot}2$ Hz in 5-alkylidene-1,3-dioxane however, clearly points to the situation[7,8] that the torsion around C_2–O must be exactly the same as in the undisturbed parent 1,3-dioxane, i.e. 63°.[23] Therefore we will adapt the values obtained in **b** and **e** and recalculate what the remaining torsion angles will become. This rough iterative process results in the sets shown under **c** and **f**. These sets are similar enough to accept them as a good final approximation.

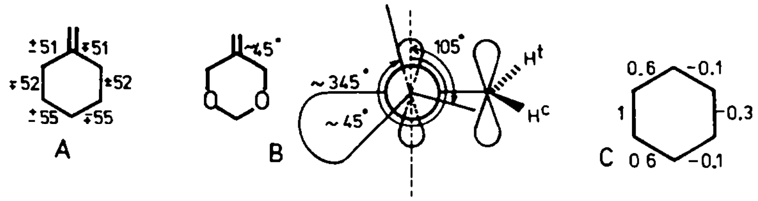

Fig. 2.

The reason for the more pronounced flattening in the 1,3-dioxanic case in comparison with cyclohexane can certainly be found in the differences in non bonded strain induced by the introduction of the exocyclic double bond. Indeed, the presence of the sp^2 carbon in a ring tends[18] to bend away the axial protons in α-position, but brings together ("reflex effect") the axial protons in β-position, an effect also observed in cyclohexanone.[18] In methylidene-cyclohexane, the approach of the latter causes some strain, and the maximal expected flattening, characterized by a torsion around C_1–C_2 of 43°, is compromised by this, resulting in a final of 51°. Because in the 5-methylidene-1,3-dioxane the β-CH_2 ring moieties have been replaced by oxygen there is no such counterbalancing effect, and we may assume that the 43° torsion can be reached.

The same value can be traced, starting from the observation that the normal valence angle θ in 2-Me-propane is 115°.[19] The relation between valence angle (θ) and adjacent torsion angle (ϕ) is then given by $\cos \frac{1}{2}\phi = 1/[2 \cos \frac{1}{2}\theta]$,[20] resulting in 43°. The change in torsion angle around one of the bonds in cyclohexane, is reflected by adapting slightly different torsion changes in the remaining bonds of the ring, however in a way that the deformation does not remain localized. From model

Barrier to ring reversal. We found a coalescence in the ^{1}H-NMR spectrum of 5-methylidene-1,3-dioxane at −158° and of 5-isopropylidene-1,3-dioxane at −161° (in freon-21) resulting in a $\Delta G^{\neq}$ of about 5·5 kcal/mole.

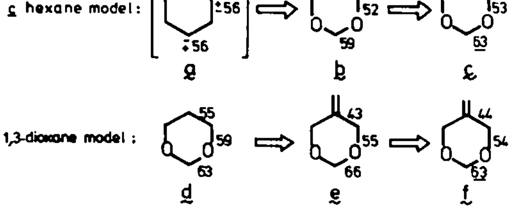

Fig. 3.

The barrier to ring reversal in methylidene cyclohexane is 7·7 kcal/mole,[24] and thus substantially higher. Therefore this is a very good indication that with respect to the carbocyclic compound, methylidene-dioxane has been even more flattened, in full accordance with our ^{1}H-NMR parameters extracted from the anancomeric model compounds in the present work.

Reduction of **1G** *and* **1H**. We have tried to gain further proof that in 4-Me-5-methylidene-1,3-dioxane the 4-Me group stands equatorial. During the preparation of **1H** in acidic medium an *equilibrium* between two forms was noticed (subsequently called the *cis*-isomer (**1H**) and *trans*-isomer (**1I**)). Of these two, the *cis*-**1H** is the most stable, as it is present in 95%. Therefore in **1G** too, the main conformation (e.g. Me-4 axial or equatorial) will be the same as in the configurational most stable isomer **1H**. Because in neither of the two compounds **1G** nor **1H**, relevant ^{1}H-NMR parameters are possible (the necessary coupling values to decide are absent), we tried to disclose their conformation, respectively configuration, through a comparative hydrogenation study.

The reduction of **1H** and **1G** leads each time to a mixture of three compounds (Fig. 4).* The distribution picture of the reduction products is almost exactly the same starting from both unsaturated compounds. In both cases the distribution reflects a kinetically controlled process (prolonged contact does not alter the relative yields). The configurations of the several reduction products were identified unambiguously by their ^{1}H-NMR spectra (Table 3). It is obvious that, as a result of the catalytic *cis*-addition to a double bond (with an approach of the catalyst's surface to the least hindered side of the substrate), the formation of 68% of the all *cis*-derivatives **5** and **4** can only be rationally explained if the 4-Me group in **1H** stands equatorial.† It is further impossible that the conformation of **1G** could be different from the partial configuration at C-4 of the most preponderent and stable isomer **1H**. The distribution in yields of the corresponding reduction products is considered to be too closely related to be the result of coincidence.*

EXPERIMENTAL

Conditions for the NMR spectral experiments were the same as previously described,[1] except that for 5-methylidene-1,3-dioxane the low temp. spectra were taken with the aid of an A-60(Varian) instrument.

5-Methylidene-1,3-dioxane and 2-Me-5-methylidene-1,3-dioxane. The isolation from 5-Me-5-I-1,3-dioxane and the parent 2-Me derivative has been described elsewhere.[1]

2-Me-, and 2,2-diMe-5-methylidene-1,3-dioxane. They were obtained, by treatment of 1,1-bis-hydroxymethyl ethylene[26] in acidic medium with acetaldehyde or acetone, in good yield, b.p. 2-Me-5-CH_2 = 1,3-dioxane: 137°/760 mm. (87%); b.p. 2,2-diMe-5-CH_2 = 1,3-dioxane: 141–145°/760 mm (70%).

4-Me-5-methylidene-1,3-dioxane. (a) 4-Me-5-CH_2Br-1,3-dioxane. A Prins condensation of formaldehyde on crotylbromide, as described[25] on allylbromide, gave 4-Me-5-CH_2Br-1,3-dioxane as the sole product (with allylbromide 5-Me-4-CH_2Br-1,3-dioxane is exclusively formed, *cf* Ref. 25). Fractionation yielded in 45% the pure compound, b.p. 101°/19 mm. (Found: C, 37·15, Br, 41·3. Calc. C, 37·0, Br, 41·8%). (b) The foregoing product (5 g) was gently refluxed for 1 hr with 10 g KOH pellets and a fraction directly distilled off. Refractionation gave in 80% yield the compound b.p. 38–40°/19 mm. (Found: C, 62·8, H, 8·9. Calc.: C, 62·6, H, 8·7$_6$%).

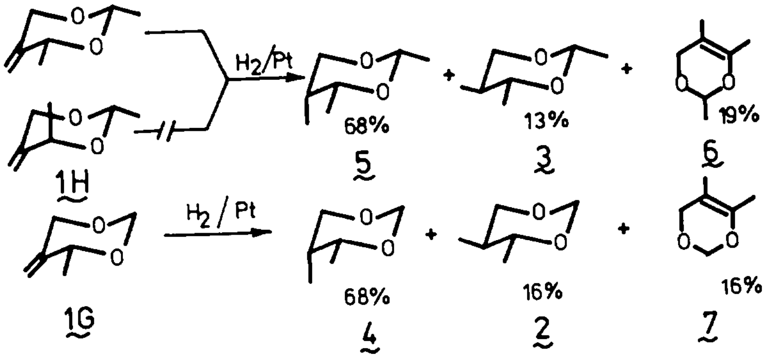

Fig. 4.

2,4-DiMe-5-methylidene-1,3-dioxane. 4-Me-5-methylidene-1,3-dioxane was refluxed for 6 hr in 10% HCl/EtOH. After cooling, the soln was neutralized with $NaHCO_3$, filtered and evaporated. To the crude diol (yield 36%), an equiv amount of depolymerized formaldehyde was added dropwise while stirring, after a few drops of 50% H_2SO_4/H_2O had been added to the diol. After extraction with ether, and washing with 10% Na_2CO_3, the ethereal layer was evaporated and the residue fractionated, b.p. 139–141°; yield 72%. (Found: C, 63·90, H, 8·8. Calc.: C, 63·6$_5$, H, 9·0$_9$%).

5-Propylidene-1,3-dioxane. Diethyl propylidene malonate was reduced with LAH following the method described.[27] Two compounds were obtained; 1,1-diMe-2,2-bis hydroxymethyl-ethylene (yield 27%) and 3-Me-2-hydroxymethylbutene (yield 34%), as proved by GC. The crude mixture was treated with formaldehyde in the usual way affording in good yield the desired dioxane, b.p. 127–130°/1 mm.

2-t-Bu-, and 2-Me-5-propylidene-1,3-dioxane. These were prepared exactly along the foregoing route, except that acetal-

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*The compounds **6** and **7** are resistent to further hydrogenation, as follows from prolonged treatments. As furthermore **1I** was only available in small quantities and could not be separated by GC, free from **1G**, we were not able to study the reduction of pure **1I**.

†As pointed out earlier, a 2-Me group will certainly be in an equatorial position, for the axial position suffers from appreciable strain with the synaxial H-4 and H-6 protons.

*One could *f.i.* argue that **1G** (with Me-4 equatorial) may be the *intermediate* during reduction. Following then the Curtin–Hammett principle, this "less-stable" intermediate could be the most reactive form, e.g. because it lacks a steric troublesome axial group that would have been present in the stable ground conformation. However, the results show that the introduction of an additional Me-2 equatorial group does not alter the reduction picture. If the most stable isomer in **1H** were indeed the one with axial Me-4, the Curtin–Hammett principle would not be applicable in this case (the "most reactive" intermediate would then be the 2,4-(pseudo) diaxial derivative, a form which is excluded). Yet, this time the ground state conformation, although energetically further removed from the critical reduction complex, would still result in exactly the same distribution pattern of reaction products. This situation is not compatible with the Hammond-principle.

dehyde, respectively privaldehyde were used. The 2-Me derivative was obtained in 47% yield, b.p. 60–62°C/17 mm, the 2-t-Bu derivative in 45% yield b.p. 132°/12 mm, purified by GC at 130° on QF$_1$.

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