ALKOXY COMPOUNDS

XXI. Synthesis, Configuration, and Conformation of Some 5-Alkoxymethyl-2,5-dialkyl-1,3-dioxanes*

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Twenty-six previously unreported 5-alkoxymethyl-2,5-dialkyl-1,3-dioxanes have been synthesized by the condensation of 2-alkoxymethyl-2-alkylpropane-1,3-diols with aldehydes. It has been shown by an analysis of the PMR spectra of these dioxanes that the 1,3-dioxanes considered are mixtures of two stereoisomers. In some cases these mixtures have been resolved into the individual isomers by vacuum fractionation in efficient columns. The configurations and conformations of the stereoisomeric 5-alkoxymethyl-2,5-dialkyl-1,3-dioxanes have been established by the NMR method; it has been shown that the lower-boiling isomers have the trans configuration and predominantly the chair conformation and the higher-boiling isomers the cis configuration and predominantly an unsymmetrical boat conformation.

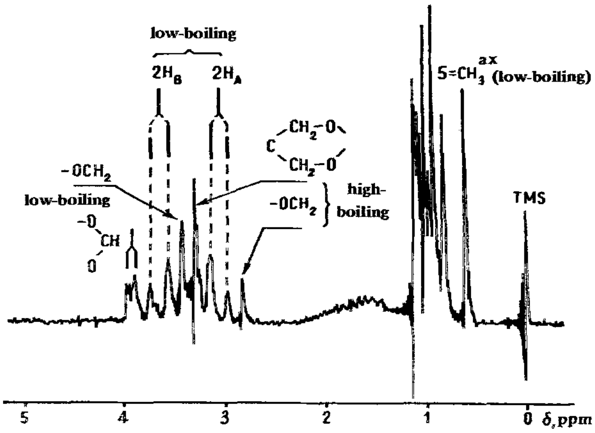
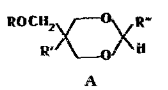
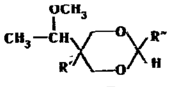


Fig. 1. PMR spectrum of a mixture of the steroisomers (cis and trans) of 5-isopropoxymethyl-2-isopropyl-5-methyl-1, 3-dioxane (XV).

Developing our previous investigations in the field of the chemistry of the 1,3-dioxanes, we have synthesized 26 previously unreported 5-alkoxymethyl-2,5-dialkyl(aryl)-1,3-dioxanes (A), the properties of which are given in Table 1. The synthesis was effected in a similar manner to the synthesis of the 5-α-alkoxyethyl-2,5-dialkyl(aryl)-1,3-dioxanes (B) that we studied previously and, as can be seen from the data of Table 1, the physical properties of the group of dioxanes mentioned are similar to the properties of substances of type B [2].



A



B

We were interested in the stereochemistry of compounds A, since they differ from B by the absence of branching of the alkoxyalkyl radical, which may lead to changes in their configuration and conformation. In actual fact, as we have established [1], fundamental differences exist in the ketal series.

The first problem which we set ourselves was to establish the existence of stereoisomers in the compounds of type A. We resolved this problem by the NMR method by analogy with our previous work [3–5]. An analysis of the PMR spectra showed that the general laws that we found in a study of series B remain valid for series A. Thus, Fig. 1 gives the spectrum of 5-isopropoxymethyl-2-isopropyl-5-methyl-1,3-dioxane (XV, Table 1).*

In the spectrum, as in the spectra of the substances of the series B studied previously with a methyl group on the carbon atom in position 5, there is a peak with an anomalously low value of the chemical shift (δ = = 0.62 ppm) belonging to this methyl group. Similar peaks are observed in all compounds A with a methyl group on the C-5 atom. As can be seen from the explanation in Fig. 1, the resonance lines of the other functional groups show that product XV is a mixture of two stereoisomers. Thus, in many respects the homologous series of compounds A has proved to be configuratively close to the series of compounds B.

By studying the integral intensities of the "anomalous" peaks in comparison with the intensities of the resonance bands of the other methyl groups and performing calculations using the formula [5]

$$X(\%) = \frac{B \cdot n}{n'(a+B)} \cdot 100 ,$$

we determined the composition of the mixtures of isomers in series B for all compounds with a methyl group in position 5. These results are given in Table 2. The spectra clearly confirm the structure of all the compounds studied.

Figure 2 gives the spectra of the 2-methyl- (II) and 2-isopropyl- (IV) -5-methoxymethyl-5-propyl-1,3-dioxanes. These compounds are characterized by the absence of a methyl group in position 5 and by the presence of a methoxy group, the resonance line of which δ = 3.20 and 3.10 ppm in compound II and δ = 3.30 and 3.20 ppm in compound IV, as in the compounds of series B, can be used to establish

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*For part XX, see [7].

*The numbering of the compounds here and below in the text of the present communication corresponds to the numbering of the compounds in Table 1.

their isomeric composition. However, in the compounds of type A the resonance bands of the methoxymethyl group have another fundamental feature. In the PMR spectra, the protons of the methylene group of the CH_3OCH_2 substituent also give a sharp line similar to the line of the methoxy group, which enables this feature of the spectrum, as well, to be used to establish the ratio of the stereoisomers. It must, however, be noted that such evaluations are less accurate than determinations from the "anomalous" peak in view of the superposition of the resonance peaks of other functional groups. We have carried out similar determinations for other compounds A containing a methoxy group. The results of the determinations are given in Table 2.

Having shown the presence of stereoisomers in the substances of type A, we separated them into the individual isomers (Table 2) by rectification in efficient total-condensation columns with a number of theoretical plates equal to 37–40 and a reflux number of from 60 to 180. The completeness of the separation can be evaluated with an accuracy of about 2–3% from the PMR spectra of the individual isomers. In the majority of cases, products of adequate purity (of the order of 95% and above) were obtained. As can be seen from the data of Table 2, the differences in the physical constants of the isomers A are similar to the corresponding differences between the isomers of type B.

The configuration and conformations of A were determined from the PMR spectra of the protons of the individual isomers. Figure 3 gives the PMR spectra of the low-boiling Ia and the high-boiling Ib isomers of 5-methoxymethyl-2,5-dimethyl-1,3-dioxane (I), which, as is easy to see, is the ancestor of the homologous series considered.

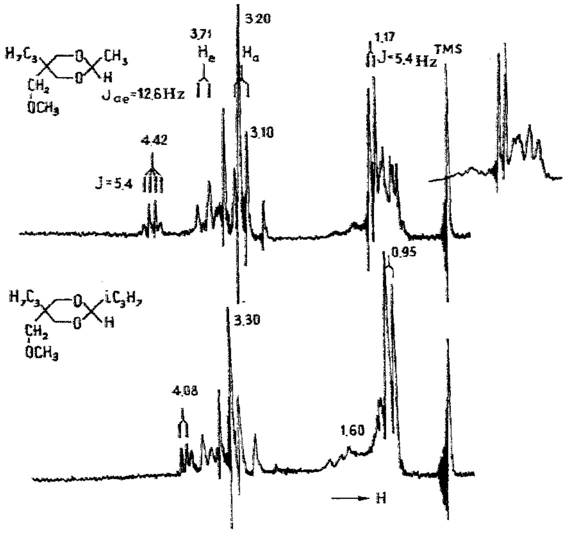

Fig. 2. PMR spectra of the steroisomeric 2,5-dialkyl-5-methoxymethyl-1,3-dioxanes (mixture of isomers): top) 5-methoxymethyl-2-methyl-5-propyl-1,3-dioxane (II); bottom) 2-isopropyl-5-methoxymethyl-5-propyl-1,3-dioxane (IV).

As can be seen (Fig. 3) in the spectrum of Ia a line with an anomalously low value of the chemical shift ("anomalous" peak) clearly appears at $\delta = 0.70$ ppm, which, as we have shown previously [3–4] indicates the axial position of this group in the stable chair conformation. It is characteristic that the "anomalous" peak in Ia is displaced in the direction of high fields to a smaller extent than in the low-boiling isomer of the simplest of the dioxanes of type B, 5-α-methoxyethyl-2,5-dimethyl-1,3-dioxane ($\delta = 0.42$ ppm). This is apparently due to the greater possibility for free rotation of the less bulky alkoxymethyl group Ia. Consequently, the pronounced shift of the resonance lines of the methyl protons of the 5-CH_3 group in the direction of high fields is due mainly to the influence of the oxygen atom of the methoxy group, this oxygen being very closely adjacent to the axial methyl and the anisotropy of the unshared pair ($2p^z$) considerably overlapping the influence of the unshared pair of the ring oxygen. The correctness of these considerations and also of the theoretical evaluation of the shifts in previous papers [3,4] is also shown by the magnitude of the chemical shift of the similar methyl in acyclic ethers and diols where there is no hindrance to the rotation of the methyl and methoxyethyl groups attached to a quaternary carbon. This shift is $\delta = 1.39$ ppm in methoxymethylmethylmalonate but it has a value of $\delta = 1.30$ ppm in α-methoxyethylmethylmalonate, where some steric hindrance of the free rotation of the groups mentioned is possible. A similar phenomenon occurs in the spectra of diols of the type of 2-alkoxyalkyl-2-alkylpropane-1,3-diols.

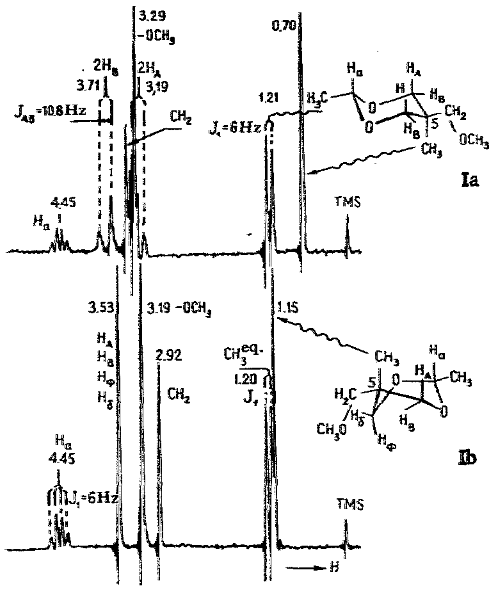

Fig. 3. PMR spectra of the stereoisomeric 5-methoxymethyl-2,5-dimethyl-1,3-dioxanes (I): Ia) low-boiling, Ib) high-boiling

The value of the shift of the spin doublet of the 2-methyl group $\delta = 1.21$ ppm ($J_{HH'} = 6$ Hz) shows the equatorial position of this group. The same conclusion can be arrived at from the value of the shift of the quadruplet of the C-2 proton which is $\delta = 4.45$ ppm ($J_{HH'} = 6$ Hz), i.e. this band is displaced in the direction of high fields as compared to the spectrum of unsubstituted 1,3-dioxane [6], which exists in a state of rapid inversion of the chair. In contrast to isomers of type B, in the isomers of type A considered, including Ia, there is another indication of the equatorial position of the alkoxyalkyl group (in the present case the methoxymethyl group) on the C-5 carbon. This is the characteristic position of the magnetic resonance line of the methylene protons of the CH_3OCH_2 group. As can be seen from the top spectrum (Fig. 3), these protons resonate at $\delta = 3.44$ ppm, i.e. the resonance line occupies its usual position (to the left of the methoxy group) as in acyclic compounds, for example, in methoxymethylmethylmalonate [1]. A quantitative evaluation of the change in the shift taking into account the anisotropy of the magnetic susceptibility of all the bonds of the dioxane ring and the effect of the electric field of the dipoles actually shows that such protons should not experience an appreciable change of the screening of the protons if the CH_2OCH_3 group occupies the equatorial position (see the tables in the previous papers [3,4]).

All these conclusions were drawn on the basis of a preliminary proof of the chair conformation which is shown by the resonance band of the methylene protons in the ring (4-CH_2 and 6-CH_2). We have shown previously that in the case of the chair conformation the resonance spectrum of these protons must correspond to a spin system of the AB type. In actual fact, in the spectrum of the low-boiling isomer, the peaks with $\delta = 3.81$, 3.64, 3.29, and 3.11 ppm form a typical AB quadruplet with nonequivalence of the axial and equatorial protons equal to $\Delta\delta = 0.52$ ppm ($J_{AB} = 10.8$ Hz). Such a considerable nonequivalence of the protons of the methylene groups of the dioxane ring is possible only if the ring exists predominantly in the chair conformation.

The PMR spectrum of the high-boiling isomer Ib (Fig. 3) differs sharply in its form from the spectrum of the low-boiling isomer Ia. Attention is attracted by the change in the chemical shift of the methyl group at C-5 ($\delta = 1.15$ ppm) and of the methylene protons of the methoxymethyl group ($\delta = 2.92$ ppm) and also by the transformation of the quadruplet of the AB system into an exceptionally sharp singlet peak with $\delta = 3.53$ ppm. This change in the spectrum is not connected with a rapid inversion of the "chair-chair" type, since on inversion the line of the CH_3 group at C-5 would have the chemical shift typical for an aliphatic methyl ($\delta \sim 0.80$ ppm); moreover, the line of the methylene protons of the $-CH_2OCH_3$ group would have the same shift as in methoxymethylmethylmalonate ($\delta = 3.68$ ppm) [1]. The shape of the spectrum of Ib shows that the isomer under consideration exists in the unsymmetrical boat conformation. The possibility of a symmetrical boat is excluded by the pronounced overlapping of the spheres of the van der Waals interaction of the atoms of the substituents in the flagstaff position. In the case of an unsymmetrical boat, the methyl in the boat-axial position at C-5 should, according to estimates made without taking the influence of the methoxymethyl group on this shift, undergo a very slight shift in the direction of lower fields. Consequently, the lines $\delta = 1.15$ ppm must be ascribed to a boat-axial methyl at C-5.

The shift in the position of the resonance of the methyl protons of $-CH_2OCH_3$ in the direction of large fields, in spite of the theoretical estimates of the change in screening, can apparently be explained by the fact that the ether oxygen of this group is close to the boat-axial C-4 hydrogen for most of the time, as can be seen in Stuart-Briegleb models.

The boat-equatorial position of the methyl at C-2 is confirmed, in the first place, by a comparison with the spectrum of 2-methyl-1,3-dioxane described by one of us [6] with the equatorial position of the methyl in the chair conformation ($\delta = 1.19$ ppm) in view of the fact that in Ib the position of the doublet mentioned is $\delta = 1.20$ ppm and this, taking into account the data of the table mentioned, must show the boat conformation, since in this conformation the change in the chemical shift of these protons in the direction of high fields must be somewhat smaller than in the chair conformation (in Ia $\delta = 1.21$ ppm) and, in the second place by a consideration of the chemical shift of the quadruplet of the hydrogen atom at C-2, the position of which ($\delta = 4.45$ ppm) remains unchanged (as predicted by the estimates) in both isomers and shows the axial position of this atom.

The complete equivalence of the protons of the CH_2 groups at C-4 and C-6 of the ring gives interesting information on the dynamics of the pulsation of the 1,3-dioxane ring. According to the estimates, the protons of the 4-CH_2 group must be appreciably nonequivalent, in contrast to the 6-CH_2 protons the nonequivalence of which must be only 0.16 ppm, as is actually the case in the spectrum of the high-boiling isomers of compounds of type B.

In the case considered, as was suggested above, the oxygen is adjacent to the CH_2 group for most of the time, while the anisotropy of its unshared pair decreases the nonequivalence of these protons. In addition, the small widths of the lines of the two methylene groups of the ring shows the presence of a pulsation of the 1,3-dioxane ring between the two "twisted forms" obtained from the unsymmetrical boat.

The results of NMR spectroscopy are confirmed by the measurements of the dipole moments of Ia ($\mu_{exp} = 1.20$ D) and Ib ($\mu_{exp} = 2.24$ D) which are in agreement with the conformations that we have adopted [1,3–5].

Thus, an analysis of the PMR spectra and a consideration of the dipole moments of Ia and Ib leads to a proof of the trans configuration for Ia and the predominant chair conformation and cis configuration of Ib and pulsations of this molecule between two "twist conformations" based on an unsymmetrical boat, which is shown on the right of Fig. 3. The configuration and conformation of the stereoisomers of compounds II, III, XIV, XV, and XVI were also determined by the PMR method. The chemical shifts and spin interaction constants J_{HH}' of the protons of the functional groups are summarized in Table 3. The rules mentioned above also apply to these compounds with the exception that the high-boiling isomers

Table 1

5-Alkoxymethyl-2-alkyl(aryl)-5-alkyl-1,3-dioxanes

Compound	R	R′	R″	Bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calculated, %		Yield, %
							found	calculated		C	H	C	H	
I	CH_3	CH_3	CH_3	52 (5)	0.9836	1.4280	41.45	41.87	$C_8H_{16}O_3$	59.80	10.81	59.97	10.00	71
II	CH_3	C_3H_7	CH_3	63 (3)	0.9765	1.4388	50.69	51.11	$C_{10}H_{20}O_3$	63.53	11.17	63.79	10.61	81
III	CH_3	$i\text{-}C_3H_7$	CH_3	70 (4)	0.9795	1.4411	50.62	51.11	$C_{10}H_{20}O_3$	63.45	11.15	63.79	10.61	82
IV	CH_3	C_3H_7	$i\text{-}C_3H_7$	90 (4)	0.9511	1.4395	59.88	60.34	$C_{12}H_{24}O_3$	66.74	11.69	66.63	11.10	82
V	CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	80 (2)	0.9689	1.4421	59.38	60.34	$C_{12}H_{24}O_3$	66.50	11.28	66.63	11.10	86
VI	CH_3	C_3H_7	C_6H_{13}	120 (3)	0.9342	1.4460	73.73	74.20	$C_{15}H_{30}O_3$	69.70	12.00	69.72	11.62	76
VII	CH_3	C_3H_7	$CH{=}CH{-}CH_3$	91 (2)	0.9862	1.4523	58.65	59.88	$C_{12}H_{22}O_3$	67.05	10.41	67.25	10.35	57
VIII	CH_3	$i\text{-}C_3H_7$	$CH{=}CH{-}CH_3$	89 (3)	0.9947	1.4570	58.67	59.88	$C_{12}H_{22}O_3$	67.09	10.49	67.25	10.35	66
IX	CH_3	C_3H_7	C_6H_5	135 (2)	1.0542	1.5030	70.16	70.60	$C_{15}H_{22}O_3$	71.70	9.00	71.97	8.80	75
X	CH_3	$i\text{-}C_3H_7$	C_6H_5	139 (4)	1.0564	1.5054	70.33	70.60	$C_{15}H_{22}O_3$	71.79	8.97	71.97	8.80	78
XI	CH_3	C_3H_7	$CH{=}CH{-}C_6H_5$	186 (4)*	—	—	—	79.37	$C_{17}H_{24}O_3$	73.58	9.55	74.00	8.75	77
XII	CH_3	$i\text{-}C_3H_7$	$CH{=}CH{-}C_6H_5$	178 (4)	1.0567	1.5320	81.04	79.37	$C_{17}H_{24}O_3$	73.69	9.42	74.00	8.75	79
XIII	$i\text{-}C_3H_7$	CH_3	CH_3	51—53 (3)	0.9385	1.4240	51.17	51.11	$C_{10}H_{20}O_3$	63.82	11.27	63.79	10.61	84
XIV	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	CH_3	81 (4)	0.9437	1.4345	59.76	60.34	$C_{12}H_{24}O_3$	66.47	11.43	66.63	11.10	94
XV	$i\text{-}C_3H_7$	CH_3	$i\text{-}C_3H_7$	75—76 (3)	0.9246	1.4290	60.31	60.34	$C_{12}H_{24}O_3$	66.68	11.63	66.63	11.10	86
XVI	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	100 (4)	0.9308	1.4380	69.05	69.58	$C_{14}H_{28}O_3$	68.50	11.76	68.79	11.50	77
XVII	$i\text{-}C_3H_7$	CH_3	$i\text{-}C_4H_9$	103—106 (6)	0.9244	1.4320	64.64	64.96	$C_{13}H_{26}O_3$	67.52	11.57	67.78	11.30	50
XVIII	$i\text{-}C_3H_7$	CH_3	C_6H_{13}	110 (4)	0.9226	1.4379	73.52	74.20	$C_{15}H_{30}O_3$	69.76	12.04	69.72	11.62	66
XIX	$i\text{-}C_3H_7$	CH_3	$CH{=}CH{-}CH_3$	105—108 (10)	0.9513	1.4440	59.83	59.88	$C_{12}H_{22}O_3$	67.20	10.65	67.25	10.35	73
XX	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$CH{=}CH{-}CH_3$	101 (3)	0.9577	1.4518	68.24	69.11	$C_{14}H_{26}O_3$	69.20	11.00	69.38	10.72	72
XXI	$i\text{-}C_3H_7$	CH_3	C_6H_5	135 (4)	1.0284	1.4920	70.39	70.60	$C_{15}H_{22}O_3$	71.81	9.15	71.97	8.80	84
XXII	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	C_6H_5	155 (5)	1.0215	1.4962	79.62	79.84	$C_{17}H_{26}O_3$	73.01	9.59	73.34	9.35	81
XXIII	$i\text{-}C_3H_7$	CH_3	$CH{=}CH{-}C_6H_5$	179 (5)	1.0321	1.5190	81.26	79.37	$C_{17}H_{24}O_3$	73.90	9.29	73.88	8.70	79
XXIV	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$CH{=}CH{-}C_6H_5$	198 (5)	1.0240	1.5195	90.31	88.60	$C_{19}H_{28}O_3$	74.80	9.81	74.96	9.27	79
XXV	$i\text{-}C_3H_7$	CH_3	C_6H_4OH	156 (3)	1.0911	1.5050	72.40	72.12	$C_{15}H_{22}O_4$	67.45	8.25	67.64	8.26	73
XXVI	$i\text{-}C_3H_7$	CH_3	$C_6H_3(OCH_3)OH$	200 (4)	1.1210	1.5150	79.73	78.38	$C_{16}H_{24}O_5$	64.65	8.43	64.84	8.16	68

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*At normal pressure the compound crystallized; mp 52° C.

Table 2

Properties of the Stereoisomeric 5-Alkoxymethyl-2,5-dialkyl-1,3-dioxanes

Compound	R	R′	R″	Bp, °C (mm)	Δt°	d_4^{20}	Δd_4^{20}	n_D^{20}	Δn_D^{20}	MR_D		ΔMR_D	Ratio of the isomers	
										found	calculated		data from column distillation*	data from PMR spectra
I	CH_3	CH_3	CH_3	65 (16) 74 (19)	3.0	0.9837 0.9862	0.0025	1.4269 1.4290	0.0021	41.84 41.96	41.87	0.06 0.09	48 52	79 21
II	CH_3	C_3H_7	CH_3	66 (1) 72.5 (1)	6.5	0.9662 0.9689	0.0027	1.4367 1.4382	0.0015	51.02 51.02	51.11	0.09 0.09	60 40	71 29
III	CH_3	$i\text{-}C_3H_7$	CH_3	55 (0.5) 62 (0.5)	7.0	0.9790 0.9838	0.0048	1.4402 1.4420	0.0018	50.70 50.63	51.11	0.59 0.52	50 50	66 34
XIV	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	CH_3	69.5 (1) 78.5 (1)	9.0	0.9362 0.9402	0.0040	1.4337 1.4354	0.0017	60.13 60.09	60.34	0.21 0.25	53 47	— —
XV	$i\text{-}C_3H_7$	CH_3	$i\text{-}C_3H_7$	55.5 (1) 58.0 (1)	2.5	0.9245 0.9284	0.0039	1.4288 1.4300	0.0012	60.30 60.19	60.34	0.04 0.15	83 17	70 30
XVI	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	68.0 (1) 73.5 (1)	5.5	0.9228 0.9289	0.0061	1.4372 1.4390	0.0018	69.40 69.04	69.58	0.18 0.54	56 44	— —

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*Data obtained from a study of the refractive index of the isomers are approximate since they depend on the purity of the fraction.

Table 3

Chemical Shifts of the Protons δ and Spin Interaction Constants $J_{HH'}$ of Some Stereoisomeric 5-Alkoxymethyl-2, 5-dialkyl-1, 3-dioxanes

Compound	R	R′	R″	Chemical shifts δ* and constants $J_{HH'}$**											
				OCH_2	R		R′				R″		$\lvert O\rvert-CH_2-\lvert O\rvert$		$\lvert O\rvert-CH-\lvert O\rvert$
					CH_3	α-CH	CH_3	α-CH_2	β-CH_2	α-CH	CH_3	α-CH	H-ax.	H-equiv.	
Ia	CH_3	CH_3	CH_3	3.40	3.29	—	0.70	—	—	—	1.21 (6)	—	3.19 (10.8)	3.71 (10.8)	4.45 (6)
Ib				2.92	3.19	—	1.15	—	—	—	1.20 (6)	—	3.53		4.45 (6)
IIa	CH_3	C_3H_7	CH_3	3.41	3.20	—	0.80	~1.00	~1.00	—	1.17 (5.4)	—	?	3.71 (12.6)	4.42 (5.4)
IIb				2.90	3.10	—	0.88	~1.05	~1.05	—	1.17 (5.4)	—	3.58		4.42 (5.4)
IIIa	CH_3	*i*-C_3H_7	CH_3	3.60	3.30	—	0.86 (6.6)	—	—	~1.5 (6.6)	1.25 (6)	—	3.40 (12)	3.90 (12)	4.45 (6)
IIIb				2.98	3.20		1.01 (6.6)	—	—	2.40 (6.6)	1.25 (6)	—	3.50 (12)	3.90 (12)	4.45 (6)
XIVa	*i*-C_3H_7	*i*-C_3H_7	CH_3	3.40	—	4.30 ?	?	—	—	?	?	—	3.20 (12)	3.75 (12)	4.30 (6)
XIVb				2.91		4.30	?	—	—	?	?		3.50		4.30 (6)
XVa	*i*-C_3H_7	CH_3	*i*-C_3H_7	3.40	1.06 (4.8)	~3.40	0.62	—	—	—	0.89	~1.60	3.13 (12)	3.77 (12)	4.04 (4.2)
XVb				2.90	0.98	~3.40	1.13	—	—	—	0.89	~1.60	3.51		4.04 (4.2)

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*The chemical shifts were determined in ppm for the pure liquids relative to tetramethylsilane (TMS); accuracy of the determination ±0.3 ppm.

**The spin-spin interaction constants $J_{HH'}$ shown in parentheses are in Hz.

exist in an unsymmetrical boat conformation without pulsations between two "twist forms." This can be seen from the broader resonance line of the methylene protons at the ring which is characteristic for each of the compounds of type A considered.

EXPERIMENTAL

The starting materials for the synthesis of the 5-alkoxymethyl-2-alkyl(aryl)-5-alkyl-1, 3-dioxanes were 2-methoxymethyl-2-methylpropane-1, 3-diol [bp 92° C (2 mm), d_4^{20} 1.0599, n_D^{20} 1.4523]; 2-methoxymethyl-2-propylpropane-1, 3-diol [bp 109° C (3 mm), d_4^{20} 1.0139, n_D^{20} 1.4560]; 2-methoxymethyl-2-isopropylpropane-1, 3-diol [bp 112° C (5 mm), d_4^{20} 1.0257, n_D^{20} 1.4553]; 2-isopropoxymethyl-2-methylpropane-1, 3-diol [bp 89° C (1 mm); d_4^{20} 0.9870, n_D^{20} 1.4430]; and 2-isopropoxymethyl-2-isopropyl-1, 3-propanediol [bp 113° C (3 mm), d_4^{20} 0.9793, n_D^{20} 1.4510], and also freshly distilled or recrystallized and previously carefully dried and purified acetaldehyde, isobutyraldehyde, isovaleraldehyde, enanthaldehyde, crotonaldehyde, cinnamaldehyde, benzaldehyde, salicaldehyde, and vanillin, the constants of which coincided with those given in the literature. KU-1 cation-exchanger in the hydrogen form was used as catalyst.

The synthesis of the dioxanes of type A was carried out by the method which we used previously to obtain 1, 3-dioxanes of type B [3, 5].

Data characterizing the properties of the 5-alkoxymethyl-2-alkyl(aryl)-1, 3-dioxanes synthesized are given in Table 1.

The distillations were carried out day and night in an efficient total condensation column of 37 theoretical plates at reflux ratios of 60 (II, XIV, XV), 90 (XVI), 100 (I), and 180 (III). The distillations were usually carried out with ~40 g of the mixture of isomers and from 16 to 18 fractions were collected, the first and last 6–7 fractions containing the individual isomers (see Table 2).

The PMR spectra were taken under the conditions that we have described previously [1] at a proton resonance frequency of 60 MHz and a temperature of 21° C on a spectrometer of type PYa-2303 built by SKB AP AN SSSR [Special Design Bureau, Academy of Sciences of the USSR]. The time for recording the spectra was 500 sec and the rate of sweep of the magnetic field was 0.2 mOe/sec.

The dipole moments were measured and calculated by L. K. Yuldasheva and R. Arshinova, to whom the authors express their hearty thanks.

REFERENCES

1. Yu. Yu. Samitov, G. I. Goryashina, A. V. Bogatskii, and O. S. Stepanova, KhGS [Chemistry of Heterocyclic Compounds] (in press), 1968.

2. A. V. Bogatskii and N. L. Garkovik, ZhOKh collection: Problems of Organic Synthesis [in Russian], 42, 1965.

3. A. V. Bogatskii, Yu. Yu. Samitov, and N. L. Garkovik, ZhOrKh, 2, 1335, 1966.

4. A. V. Bogatskii, Yu. Yu. Samitov, N. L. Garkovik, and S. A. Andronati, KhGS [Chemistry of Heterocyclic Compounds], 3, 195, 1967.

5. Yu. Yu. Samitov, N. L. Garkovik, A. V. Bogatskii, and S. A. Zolotareva, KhGS [Chemistry of Heterocyclic Compounds] (in press), 1968.

6. Yu. Yu. Samitov and R. M. Aminova, ZhSKh, 5, 207, 1964.

7. A. V. Bogatskii, A. I. Gren, Zh. I. Bezgudova, O. S. Stepanova, D. B. Furman, G. V. P'yankova, T. K. Chumachenko, and E. B. Petrenko, KhGS [Chemistry of Heterocyclic Compounds], collection 1, 89, 1967.

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