INVESTIGATIONS OF POLYFUNCTIONAL OXIDES

V.* PMR SPECTRA, CONFIGURATIONS, AND CONFORMATIONS OF 2,2,4-TRIALKYL-5-(2-CARBOALKOXYVINYL)-1,3-DIOXOLANES AND 2,2,4-TRIALKYL-5-(2-CARBOALKOXYETHYL)-1,3-DIOXOLANES

Yu. Yu. Samitov, L. P. Glushko,
M. S. Malinovskii, and N. I. Pokhodenko

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The reaction of esters of 4,5-epoxy-2-hexenoic acid with ketones in the presence of acid catalysts gives 2,2,4-trialkyl-5-(2-carboalkoxyvinyl)-1,3-dioxolanes, the hydrogenation of which gives the corresponding saturated dioxolanes. The conformations and configurations of the dioxolanes obtained were studied by means of their PMR spectra.

We have previously studied the reduction of esters of 4,5-epoxy-2-hexenoic acid with lithium aluminum hydride and hydrogen in the presence of Raney nickel [2]. The present paper is devoted to the preparation of dioxolanes I-VII (Table 1) by the reaction of esters of 4,5-epoxy-2-hexenoic acid with ketones in the presence of acid catalysts (BF_3 and $FeCl_3$). The structures of the synthesized compounds were established by hydrolysis and IR and PMR spectroscopy. The IR spectra of the compounds contain absorption bands at 1025-1055 cm^{-1}, which are characteristic for acetals, at 1715 cm^{-1}, which are characteristic for $C=O$ bonds, and at 1650 cm^{-1}, which are characteristic for the $C=C$ bond. The absorption band at 840 cm^{-1} characteristic for epoxides is absent.

Dioxolanes VIII-XIII (Table 2) were obtained by hydrogenation of I-VI with hydrogen in the presence of Raney nickel. The absorption band characteristic for the $C=C$ bond is absent in the IR spectra of these compounds, while the absorption band characteristic for acetals (1046 cm^{-1}) is retained. The configurations and conformations of the compounds obtained were established by means of PMR spectroscopy. The resonance of the olefin protons in the PMR spectrum of dioxolane I appears as a typical quartet with a vicinal J_{CD} constant of 15.2 Hz (Fig. 1). This value is typical for a trans orientation of the interacting protons attached to the double bond. It can further be seen that the doublet of the H_C proton experiences subsequent splitting with the H_B proton with a J_{CB} constant of 6.0 Hz. This value attests to the fact that the conformation relative to the C_3-C_4 bond is not s-trans or s-cis, since, according to the Karplus–Conroy angular correlation, the vicinal constant should be considerably larger for such conformations. The J_{CB} = 6.0 Hz value can be explained by the fact that the structural fragments of the C_3-C_4 bond undergo free rotation. The J_{BC}^{trans} constant for the s-trans conformation should be on the order of 12-14 Hz, while J_{BC}^{gauche} is about 2.5 Hz for the gauche conformations. Thus, on averaging with the rotation, we obtain $J_{BC} = \frac{1}{3}(2\,{}^3J_{BC}^{gauche} + {}^3J_{BC}^{trans}) \simeq$ 5.6-6.3 Hz, which is in good agreement with the observed value of 6.0 Hz.

The configuration of the substituents relative to the 1,3-dioxolane ring can also be established from the vicinal constants for the H_B and H_A protons. From the explanations in Fig. 1, it can be seen that these protons interact with a constant of 6.3 Hz. It is known [3] that the trans constant for small rings, including five-membered rings, is lower than the cis constant. We will therefore assume that the J_{AB} constant of 6.3 Hz indicates a trans orientation of the substituents. It can be seen from the PMR spectrum that the protons of the gem-dimethyl grouping have considerable nonequivalence, which decreases practically in-

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*See [1] for communication IV.

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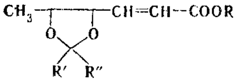
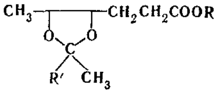
TABLE 1



Compound	R	R′	R″	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calc.%		Yield, %
							found	calc.		C	H	C	H	
I	CH_3	CH_3	CH_3	81—82 (2)	1,0662	1,4550	50,80	50,62	$C_{10}H_{16}O_4$	60,2	8,1	60,0	8,0	54
II	CH_3	CH_3	C_2H_5	98—100 (4)	1,0493	1,4590	55,72	55,27	$C_{11}H_{18}O_4$	61,9	8,3	61,7	8,4	56
III	C_2H_5	CH_3	CH_3	90—91 (2)	1,0397	1,4540	55,70	55,32	$C_{11}H_{18}O_4$	61,8	8,2	61,7	8,4	54
IV	C_2H_5	CH_3	C_2H_5	90—91 (1)	1,0453	1,4558	59,22	59,96	$C_{12}H_{20}O_4$	62,9	8,7	63,1	8,8	55
V	i-C_3H_7	CH_3	C_2H_5	94—96 (1)	1,0133	1,4548	64,75	64,60	$C_{13}H_{22}O_4$	64,7	9,3	64,4	9,1	51
VI	C_6H_5	CH_3	CH_3	164—166 (6)	1,1082	1,5120	68,90	70,91	$C_{15}H_{18}O_4$	69,0	6,9	68,7	6,9	37
VII	i-C_3H_7	C_2H_5	C_2H_5	101—103 (1)	1,0025	1,4600	69,39	69,29	$C_{14}H_{24}O_4$	65,3	9,1	65,6	9,4	48

TABLE 2



Compound	R	R′	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calc., %		Yield, %
						found	calc		C	H	C	H	
VIII	CH_3	CH_3	70—71 (1)	1,0286	1,4340	51,12	51,10	$C_{10}H_{18}O_4$	59,6	8,9	59,4	9,0	84
IX	CH_3	C_2H_5	84—85 (1)	1,0152	1,4380	55,94	55,75	$C_{11}H_{20}O_4$	61,0	9,3	61,1	9,3	96
X	C_2H_5	CH_3	70—72 (1)	—	1,4305			$C_{11}H_{20}O_4$	61,3	9,4	61,1	9,3	83
XI	C_2H_5	C_2H_5	86—88 (3)	1,0094	1,4362	59,59	60,44	$C_{12}H_{22}O_4$	62,9	9,4	62,6	9,6	80
XII	i-C_3H_7	C_2H_5	112—114 (10)	0,9814	1,4350	64,57	65,08	$C_{13}H_{24}O_4$	64,1	9,9	63,9	9,8	87
XIII	C_6H_5	CH_3	150—152 (4)	1,0798	1,4930	70,99	69,38	$C_{15}H_{20}O_4$	68,3	7,9	68,2	7,6	60

significantly as the temperature rises ($\Delta\nu$ = 13.8 Hz at 22° and 13 Hz at 100°). It would seem that this can be explained by the fact that the conformation of the 1,3-dioxolane ring is fixed and has the form of either a half chair or an envelope. We think that this assumption is incompetent, and that the dioxolane ring is in a state of conformational isomerization, while the nonequivalence of the methyl protons is due to a different effect of the substituents on the chemical shift of the methyl groups of the gem-dimethyl grouping; i.e., these methyl groups are diastereotopic with respect to the asymmetrical 5-C carbon. We next consider the conformation of the methoxycarbonyl group relative to the unsaturated bond. The fact that the H_C and H_D protons have considerable nonequivalence ($\Delta\delta$ = 0.75 ppm), during which the H_C proton is shifted to lower field, indicates that the H_C proton is subject to considerable paramagnetic anisotropic influence of the CO group. This is possible if it is not in conjugation with the double bond. Consequently, we can here assume the s-cis conformation of the unsaturated fragment.

The structures of the saturated 1,3-dioxolanes were also established by an analysis of the PMR spectra. As an example, we will consider the spectrum of 2,2,4-trimethyl-5-(2-carbomethoxyethyl)-1,3-dioxolane (Fig. 2). We identified the resonance lines by double homonuclear resonance. It can be seen from Fig. 2 that the orientation of the substituents relative to the 1,3-dioxolane ring is retained during reduction, but the chemical shifts of the H_A and H_B protons are reversed. It seemed of interest to us to examine the conformation relative to the C_2-C_3 single bond. It might have been expected from the general concepts of

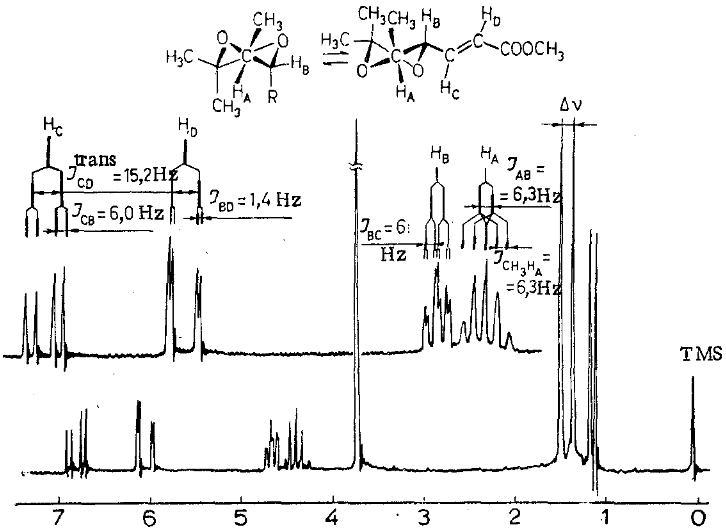


Fig. 1. PMR spectrum of 2,2,4-trimethyl-5-(2-carbomethoxyvinyl)-1,3-dioxolane (at 23°C).

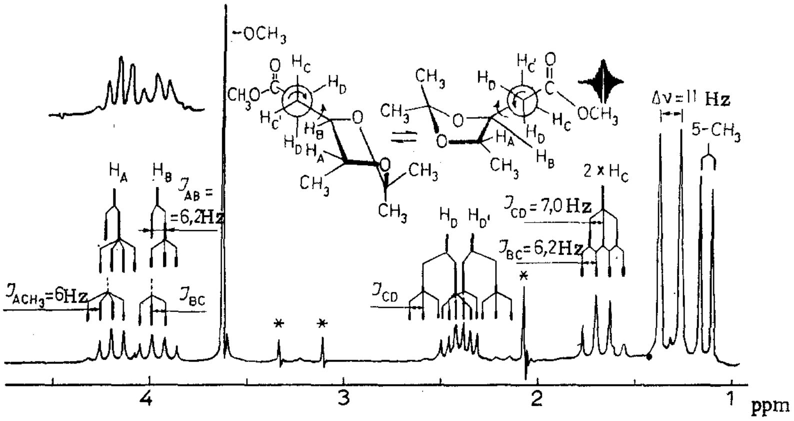
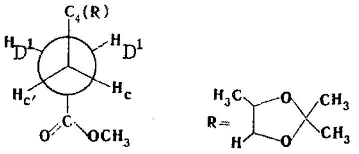


Fig. 2. PMR spectrum of 2,2,4-trimethyl-5-(2-carbomethoxyethyl)-1,3-dioxolane. The results with respect to total ($\gamma H_2/2\pi \gg J_{HH'}$) proton–proton double resonance are presented above the major spectrum. The asterisks designate the lines affiliated with impurities.

conformational analysis that the protons of the α-CH_2 group should be magnetically nonequivalent, since they are diastereotopic with respect to the asymmetrical 4-C carbon atom. However, it is apparent from the PMR spectrum (Fig. 2) that the character of the multiplicity of the δ = 1.65 ppm signal, which is affiliated with the α-CH_2 group, attests to equivalency of the protons of this group. Thus, in this concrete case, the effect of the anisotropy of the diamagnetic susceptibility of the bond and atoms, as well as the effect of the electrical field of the dipoles on the nuclear magnetic shielding constant of the protons of the α-CH_2 group, is apparently compensated (H_C and $H_{C'}$ protons, Fig. 2). The assignment of the quartet band at 1.65 ppm to the α-CH_2 group is confirmed by homonuclear double resonance. As seen from Fig. 2, when the nuclear spins of the α-CH_2 group undergo "agitation," "decoupling" of the spin interaction of these protons of the β-CH_2 group (δ = 2.38 ppm) and with the methylidyne proton of the 4-H_B group (δ = 3.94 ppm) is observed.

The PMR and nuclear magnetic double resonance spectra of the protons of the β-CH_2 group are evidence for nonequivalence of the H_D and $H_{D'}$ protons, which may be due, it would seem, to the existence of the predominant trans conformation of the C_2–C_3 ethane fragment at room temperature (23°). As the temperature of the sample rises, the contribution of the other conformation increases, and, as a result of averaging of the chemical shift, the band at 2.38 ppm should have become a triplet (Fig. 2), which is contrary to the experimental observation. At 100°, the character of the multiplet splitting of the band of the

β-CH_2 group is retained, and the nonequivalence of the gem-dimethyl grouping does not change: $\Delta\nu$ (+100°) = 11.0 Hz. This indicates the diastereotopic character of the H_D and $H_{D'}$ protons, which are two σ bonds away from the asymmetrical 4-C carbon atom.



The dioxolane ring is configurationally similar to the unsaturated 1,3-dioxolanes described above. The similar characteristic resonances of the H_A and H_B protons in this compound are graphically indicative of this. The dioxolane rings in saturated and unsaturated compounds are apparently conformationally different. Inversion of the ring between the envelope conformations occurs in saturated compounds.

EXPERIMENTAL

PMR Spectra. The PMR spectra were recorded with a Varian HA-100 D spectrometer during partial scanning of the spectra. The resonance conditions were stabilized from the line of tetramethylsilane (TMS) or chloroform, which were the internal standards. The samples used were 15% (by volume) solutions in CCl_4. The nuclear magnetic double resonance experiments were performed by the side-band method with a Muirhead decade generator. The esters of 4,5-epoxy-2-hexenoic acid were obtained by epoxidation of the appropriate esters of 2,4-hexadienoic acids [2].

2,2,4-Trimethyl-5-(2-carbomethoxyvinyl)-1,3-dioxolane (I). A 7.4-g (0.052 mole) sample of methyl 4,5-epoxy-2-hexenoate was added dropwise with stirring to a solution of 0.5 g of ferric chloride in 10 ml of acetone. The temperature was observed to rise to 50°. The reaction mass was then heated at 50-60° for 2 h, cooled, and washed with saturated potassium carbonate solution. The precipitate was removed by filtration and washed with ether. The ether extracts were dried with anhydrous potassium carbonate, and the solvent was removed by distillation in vacuo (with a water pump). The residue was fractionated under higher vacuum to give 5.2 g (50%) of dioxolane I. Dioxolanes II-VII were similarly obtained.

2,2,4-Trimethyl-5-(2-carbomethoxyethyl)-1,3-dioxolane (VIII). A 3.7-g (0.018 mole) sample of dioxolane I in 30 ml of absolute alcohol was hydrogenated under the usual conditions in the presence of 3.2 g of Raney nickel. The hydrogenation was complete in 3 h after absorption of the theoretically calculated amount of hydrogen. The catalyst was removed by filtration, the alcohol was removed by distillation, and the residue was vacuum fractionated to give 3 g (81%) of dioxolane VIII. Dioxolanes IX-XIII were similarly obtained.

Hydrolysis of 1,3-Dioxolane I. A 1-g sample of I was heated with 20 ml of 5% H_2SO_4. The acetone formed was isolated as the p-nitrophenylhydrazone with mp 149°. The product did not depress the melting point of a genuine sample of the hydrazone.

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