ISOMERIZATION OF 2-TRICHLOROMETHYL-4-METHYLENE-1,3-DIOXOLANES

A. S. Atavin, A. N. Mirskova, T. S. Proskurina, V. K. Voronov, and G. A. Kalabin

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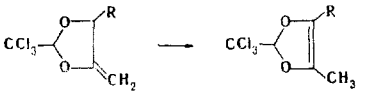
The thermal isomerization of 2-trichloromethyl-4-methylene-1,3-dioxolanes was studied. This reaction may serve as a convenient method for the preparation of 2-trichloromethyl-4-methyl-5-alkyl(aryl)-1,3-dioxols.

Unsaturated cyclic acetals of chloral that contain exo- and endocyclic double bonds are of interest as polyfunctional monomers for the synthesis of polymers with thermal and hydrolytic stability.

Continuing our systematic investigation of the properties of 2-trichloromethyl-4-methylene-1,3-dioxolanes (I) [1-3], we have observed that they are capable of isomerization to 1,3-dioxols II:



I a-c II a-c

a R=H; b R=CH_3; c R=C_6H_5

The reaction proceeds on heating without the use of any initiators. The experimental results were evaluated by PMR spectroscopy (Table 1). The assignment of the signals to the cis and trans isomers Ib

TABLE 1. Parameters of the PMR Spectra of 1,3-Dioxolanes Ia-c and 1,3-Dioxols IIa-c

Compound	δ, ppm						J, Hz
	2-H	5-H	4α-H (cis to 5-C)	4β-H (trans to 5-C)	CH_3	R	
Ia	5,47	4,59 (cis to CCl_3)	3,80	4,42		4,37 (trans to CCl_3)	$(J_{4\alpha,5}+J_{4\alpha,R})/2=1,8$; $J_{5,R}=11,2$; $(J_{4\beta,5}+J_{4\beta,R})/2=2,3$; $J_{4\alpha,4\beta}=2,9$
Ib cis	5,43	4,88	3,88	4,40		1,43	$J_{5,R}=6,2$; $J_{4\alpha,4\beta}=3,0$; $J_{4\alpha,5}=J_{4\beta,5}=2,0$
Ib trans	5,49	5,01	3,88	4,40		1,38	
Ic cis	5,53	5,46	3,63	4,45		7,30	$J_{4\beta,5}=2,0$; $J_{4\alpha,5}=2,2$; $J_{4\alpha,4\beta}=2,8$
Ic trans	5,71	5,78	3,78	4,51		7,30	$J_{4\beta,5}=2,2$; $J_{4\alpha,5}=1,7$; $J_{4\alpha,4\beta}=2,8$
IIa	5,89				1,81	6,03	$J_{R,CH_3}=1,6$
IIb	5,78				1,76	1,76	
IIc	5,96				2,12	7,28	

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TABLE 2. Dependence of the Degree of Isomerization of Dioxolane Ib on the Temperature

Temp., °C	Dioxolane Ib, %		Dioxol IIb, %
	cis isomer	trans isomer	
50—110	65	35	0
130	54	43	3
140	36	46	5
150	12	48	40
170	21	35	44
180	9	30	61
200	0	10	90
80*	53	42	5

* The experiment was carried out for 5 h.

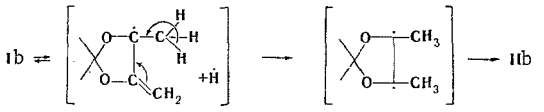
and Ic (relative to the orientation of the substituents in the 2 and 5 positions) was made starting from the 2-H and 5-H chemical shifts and is in agreement with the previously detected long-range spin-spin coupling constants characteristic for a trans orientation of these protons [4].

It was found from an evaluation of the integral intensities of the signals that the cis-to-trans isomer ratios for Ib and Ic are 65 : 35 and 75 : 25, respectively.* The components of the 5-H signal (δ 5.01 ppm) of the trans isomer Ib are broadened in comparison with the resonance lines of the other signals; this is a consequence of the long-range spin-spin coupling in the H—C(CCl_3)—O—C—H fragment. For the same reason the 2-H signal of the trans isomer (δ 5.49 ppm) is a doublet, which is converted to a singlet on suppression of the signal at δ 5.01 ppm (double-resonance method).

The results of the isomerization of 2-trichloromethyl-5-methyl-4-methylene-1,3-dioxolane (Ib) on heating in sealed ampuls at 50-200° for 30 min are presented in Table 2. Intensive formation of the endo isomer of IIb is observed only above 150°, and the isomerization of the cis isomer of Ib proceeds more readily than that of the trans isomer. Increasing the temperature to 220° entails resinification of the reaction mixture. At 200°, the yield of isomerization products was 85%. At 130-150°, the curve of the dependence of the relative percentage of the trans isomer of Ib on the temperature has a maximum, which attests to an increase in the fraction of it present as against the sharp decrease in the fraction of cis isomer Ib.

Consumption of the cis isomer of Ib may apparently occur in two directions — in the formation of dioxol IIb and in conversion to the trans isomer. To confirm the latter assumption, we carried out the isomerization of Ib at 80° for 5 h. The results (Table 2) unambiguously attest to conversion of the cis isomer to the trans isomer. It follows from Fig. 1 that dioxol IIb forms from both the cis and trans isomers of Ib.

The mechanism of the isomeric transformation of 2-trichloromethyl-5-methyl-4-methylene-1,3-dioxolane can be represented in the following way: the reaction begins with detachment of a proton as a result of homolysis of the C—H bond in the 5 position of the dioxolane ring; the resulting radical is stabilized by conjugation with the π electrons of the double bond and the methyl group attached to the reaction center; this leads to intermediate structure A, which is close to that of a planar pyramid [5]. In the second step of the reaction, recombination of radicals is possible either by addition of hydrogen to the site of its detachment (in this case both frontal attack and approach from the "rear" with respect to the central atom can be realized) or by addition of hydrogen to the opposite end of the conjugated system (B). In the first case the cis and trans isomers of Ib are formed, while dioxol IIb is formed in the second case:



A B

The small amount of the trans isomer of Ib that is formed from the cis isomer under conditions that coincide with the most intensive increase in the concentration of IIb (Fig. 1) is apparently a consequence of isomerization in the reaction center.

* The assignment of the protons to the cis and trans isomers for Ic was made in analogy with Ib, but the observed differences in the same spin-spin coupling constants in the isomers of Ic require special experiments for the definitive solution of this problem.

TABLE 3. Relative Percentage (%) of Dioxolanes and Dioxols in the Isomerization of Ia-c (heating time 30 min)

Temp., °C	Ia	IIa	Ib (cis + trans)	IIb	Ic (cis + trans)	IIc
150	88	12	60	40	30	70
170	77	23	56	44	0	100
200	28	72	10	90	0	100

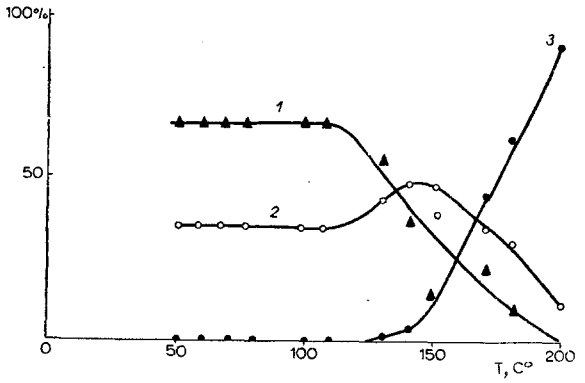


Fig. 1. Dependence of the relative percentage of cis and trans isomers of 2-trichloromethyl-5-methyl-4-methylene-1,3-dioxolane (Ib) and 2-trichloromethyl-4,5-dimethyl-1,3-dioxol (IIb) on the temperature: 1) cis isomer of Ib; 2) trans isomer of Ib; 3) 1,3-dioxol IIb.

One should expect that the stability of the final products will increase on passing from IIa to IIb and IIc. In fact, the results of the isomerization of 2-trichloromethyl-4-methylene-1,3-dioxolane (Ia) and its 5-substituted analogs (Table 3) under comparable conditions demonstrate that the effect of a methyl substituent – and, to an even greater degree, a phenyl substituent – in Ib and Ic is manifested in acceleration of the isomerization to the corresponding 1,3-dioxols IIb,c.

In the isomerization of Ic, the cis isomer is more readily converted to IIc than the trans isomer, as attested to by a comparison of the composition of the reaction mixture (after heating at 150° for 30 min) – 15% of the cis isomer of Ic, 15% of the trans isomer of Ic, and 70% of IIc – with the isomeric composition of the starting compound.

To confirm the homolytic mechanism for the isomerization of 1,3-dioxolanes Ia-c to dioxols IIa-c, we carried out experiments in the presence of catalytic amounts of hydrogen peroxide (at 130° for 30 min) with Ia and in the presence of UV irradiation (at 65° for 6 h) with Ic. According to the PMR spectrum, the reaction mixture in the first case consisted of 26% Ia and 74% IIa (95% yield), while only 12% IIa was formed without a catalyst at 150° for 30 min (Table 3). In the second case, the reaction mixture consisted of 15% of the trans isomer of Ic and 85% of IIc. This result also confirms the noted fact of the greater ease of isomerization of the cis isomer.

The investigated reaction may serve as a convenient method for the preparation of previously difficult-to-obtain [6, 7] 2-trichloromethyl-1,3-dioxols.

The structure of 2-trichloromethyl-1,3-dioxols IIa,b is confirmed by their IR spectra, in which the absorption bands at 1708 and 1724 cm^{-1} correspond to the vibrations of the endocyclic double bond, while, as has been shown in [8], the doublet at 1665 and 1700 cm^{-1} in the spectra of starting Ia,b corresponds to the vibrations of the exocyclic double bond. A strong band at 1672 cm^{-1} with a shoulder on the high-frequency side (~1692 cm^{-1}) is characteristic for the C = C bond in Ic. Two intense bands at 1683 and 1713 cm^{-1} appear in the IR spectra on passing to isomerization product IIc.*

EXPERIMENTAL

The PMR spectra in 20 mole % solutions in CCl_4 were recorded at 30° with a BS 487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The integral intensities of the signals were calculated with an accuracy of up to 2%. The IR spectra were recorded with a UR-10 spectrophotometer.

2-Trichloromethyl-5-phenyl-4-methylene-1,3-dioxolane (Ic). A 15-g (0.1 mole) sample of chloral was added to 15.4 g (0.11 mole) of 2-phenyl-1-propyn-3-ol, after which 1 g of red mercuric oxide was added and the mixture was heated. At 110°, the mixture began to effervesce and took on a gray color. It was then heated at 70° for 2 h. The precipitated mercury was removed by filtration, and the filtrate was vacuum distilled to give 19.6 g (60%) of Ic with mp 54° (from hexane) and bp 110° (2 mm). Found: C 46,9; H 3.2; Cl 37.9%. $C_{11}H_9Cl_3O_2$. Calculated: C 47.2; H 3.2; Cl 38.1%.

Compounds Ia and Ib were obtained via the method in [1].

Isomerization of 1,3-Dioxolanes Ia-c to 1,3-Dioxols IIa-c. A 3-g (0.01 mole) sample of Ic was heated in a sealed ampul at 160° for 30 min. Distillation of the contents gave 2.7 g (90%) of IIc with mp 65° (from hexane) and bp 119-120° (2 mm).

Heating 3 g (0.014 mole) of Ia in a sealed ampul at 200° for 30 min gave 2.4 g (80%) of a mixture consisting of 72% IIa and 28% Ia. Heating 4 g (0.016 mole) of Ib under similar conditions gave 3.4 g (85%) of a mixture consisting of 90% IIb and 10% Ib.

* According to the PMR spectrum, this compound contains more than 98% IIc.

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